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METAL OXIDE MATERIALS AND DECONTAMINATION METHODOLOGY

FINAL REPORT

AUTHOR: DR. CRAIG L. HILL

1/15/91

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REPORT

A. Statement of problem studied. The focus of this ARO contract was the investigation of metal oxide materials, and in particular d^0 transition metal oxide clusters (polyoxometalates), as catalysis for the decontamination of chemical warfare (cw) agents and model compounds of these agents. Secondary goals dealt with delineation of the unusual reactivities exhibited by some polyoxometalate excited states and their abilities to alter unactivated C-H bonds in unusual if not unprecedented ways.

B. Summary of the most important results. Many significant results consistent with the goals of the research were in fact achieved. These include the following: (1) the formulation of polyoxometalate-based catalytic systems for the photochemical decontamination of cw agents and simulants; (2) the formulation and development of systems for the high-conversion high-selectivity photochemical replacement of unactivated C-H bonds with other groups; (3) the development of catalytic systems for the homogeneous selective dehalogenation of halocarbons (one primary halocarbon toxin is mustard = HD; structure: $\text{Cl}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{Cl}$); (4) quantitative comparison of semiconductor metal oxides and the corresponding polyoxometalates as catalysts for photochemical degradation of organic materials over a range of conditions.

The principal catalysts in this work are polyoxometalates. Polyoxometalates are condensed oligomeric aggregates composed of d^0 transition metal (TM) and oxide ions held together in well defined molecular geometries only by metal-oxygen bonds. These latter complexes occur in two large generic categories, the isopolyoxometalates (or isopoly compounds) which contain only TM and oxide ions, and the heteropolyoxometalates (or

large generic categories, the isopolyoxometalates (or isopoly compounds) which contain only TM and oxide ions, and the heteropolyoxometalates (or heteropoly compounds, of which one large subset is the heteropoly acids) which contain one or more TM or main group "heteroatoms" in the structure in addition to the constitutional and more abundant d⁰ TM and oxide ions. Figure 1 illustrates in polyhedral notation one representative isopoly compound, decatungstate, and one representative heteropoly compound, the "Keggin" ion. Most of the polyoxometalates are very low in

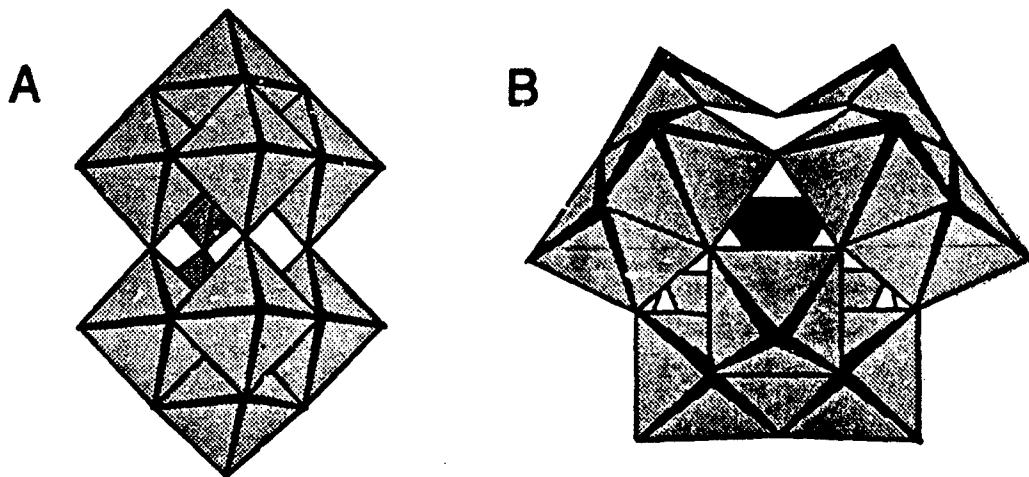


Figure 1. Structures in polyhedral notation of representative polyoxometalates. A: the isopolytungstate, $W_{10}O_{32}^{4-}$, (D_{4h} point group symmetry); B: the Keggin heteropolytungstate, $\alpha\text{-}PW_{12}O_{40}^{3-}$, M = Mo or W (T_d point group symmetry). The P^{5+} "heteroatom" in the Keggin structure is more darkly shaded and occupies a tetrahedral hole in the center of the structure. In polyhedral notation each octahedron represents one metal atom surrounded by 6 oxygen atoms (or a tetrahedron in the case of the 4-coordinate central atom in B). The metal atom in each octahedron is displaced toward its one terminal oxo group. The metal atom is not seen directly in polyhedral notation.

toxicity and their potential deployment in large quantities should have minimal deleterious effects on the environment. Several classes of polyoxometalates can be prepared in quantity from accessible starting materials while a few are less than straightforward to prepare.

The results of early collaborations between the PI's group at Emory and staff at CRDEC dealt with the photodecontamination of actual cw agents catalyzed by polyoxometalates of tungsten and led to the writing of our original ARO contract application.¹ In effect, it was determined that $H_3PW_{12}O_{40}$ rapidly and catalytically oxidatively degraded the G agents and VX to some extent. Subsequent work in the following months in 1987 and 1988 established that much of the removal of VX was due to formation and precipitation of the protonated VX of the $PW_{12}O_{40}^{3-}$ complex. Later it was shown that the decatungstate complex, $W_{10}O_{32}^{4-}$, is far more

reactive in the photochemical catalytic degradation of VX than $PW_{12}O_{40}^{3-}$ and facilitates complete removal of this fairly robust cw agent in the presence of air (21% O_2) and near UV and blue light.² At the same time that some polyoxometalate systems were established to be effective for the catalytic photochemical oxidation of cw agents and some highly inert organic materials including alkanes, some other polyoxometalate systems were developed that catalyzed the thermal oxidation of alkanes and other organic substrates using sources of reduced oxygen such as alkyl hydroperoxides. All these new photochemical and thermal systems developed in our laboratory required rigorous examination – the fundamental energetic and mechanistic features of these new catalytic processes needed to be established so that the scope and potential of these chemistries could be defined.

Reference 3 established some of the features of a thermal catalytic oxidation systems and introduced the use of CBr_4 and other additives to effect the replacement of unactivated C-H bonds with C-halogen or C-nitrogen bonds. The abstract for reference 3, reproduced immediately below summarizes the salient points of this chemistry.

Abstract. A catalytic system has been developed that can produce reasonable yields of *N*-alkylacetamides directly from alkanes by replacement of unactivated carbon-hydrogen bonds with carbon-nitrogen bonds. This system is constituted by an oxidatively resistant heteropolytungstate complex, $PW_{11}(M)O_{39}^{5-}$, $M = Co^{II}$ and Mn^{II} , 1-M as the catalyst, *t*-butyl hydroperoxide as the oxidant, tetranitromethane, and substrate alkane in acetonitrile. The related systems where tetranitromethane has been replaced by the tetrahalomethanes, CX_4 , $X = Cl$ or Br , catalytically produce the corresponding alkyl halides from alkanes with very high selectivities. Although product distribution, kinetic isotope effect, and other studies suggest that the substrate activation process is radical in nature, the *N*-alkylacetamides are likely formed from carbonium ions generated by oxidation of intermediate alkyl radicals under the reaction conditions.

As some of the thermal oxidative degradation chemistry catalyzed by polyoxometalate derivatives was similar to the metalloporphyrin chemistry that we and many other groups had investigated in the early and mid 1980s, we turned to a closer examination of the C-halogen and C-nitrogen bond forming processes catalyzed by metalloporphyrins in the presence of oxygen donors. Reference 4 is thorough study of some the selectivities in this chemistry. The abstract for reference 4 is given immediately below.

Abstract: Upon treatment of the two-phase systems, Mn tetraarylporphyrin, and alkane (organic phase) / Na^+X^- (aqueous phase), with iodosylarenes, both alcohols and alkyl azides (or halides), $X^- =$ halide or azide, are formed from the alkane substrates. The Mn porphyrin functions as a catalyst for alkane oxygenation and a phase transfer catalyst for X^- . Catalytic functionalization of the exemplary caged alkane, adamantane, by a variety of

these two-phase systems as function of the reaction conditions has been examined. The results reported here allow for the first time, an assessment of the relationship between the electronic and structural features of the metalloporphyrin catalysts and their selectivity with respect to the replacement of unactivated alkane carbon-hydrogen bonds with oxygen versus nonoxygen (halide or azide) functional groups. Of the first-row transition metal metalloporphyrins, only those of manganese are active for both the cleavage of unactivated alkane C-H bonds and replacement of these bonds by halogen or nitrogen-based groups. The oxygen donors that give the highest yields of these nonoxygenated products are the iodosylarenes. Examination of adamantane functionalization by iodosylarenes catalyzed by eight different manganese tetraphenylporphyrin derivatives, whose porphyrin ligands vary widely in the electron donating ability, establishes that the relative tertiary: secondary C-H cleavage selectivities are minimally affected by such electronic effects. In contrast, the selectivity for incorporation of the nonoxygen versus oxygen functions is substantially affected by the electron donating ability of the catalyst porphyrin rings. The more electron-withdrawing the porphyrin ring, and consequently the more anodic the potential of the ligated, $S = 2$, manganese(III) ion, the lower the selectivity for incorporation of the nonoxygen functions. Functionalization of adamantane catalyzed by the most electron poor manganese porphyrin complex, $Mn^{III}(F_{20}TPP)X$ is effectively selective for oxygenation. All the metalloporphyrins examined here eventually succumb to deactivation by irreversible oxidative degradation of the organic porphyrin ligand.

The experimental delineation of the catalytic photochemical oxidation systems was probed in a series of studies and papers using alkanes and cw agent analogues as substrates. Reference 5 reported unusual chemoselectivities (relative rates of reaction of different types of C-H bonds and different types of molecules) and probed the origin of these unusual selectivities. The abstract of reference 5 follows:

Abstract The excited states of a representative heteropolytungstate, α - $PW_{12}O_{40}^{3-}$, and a representative isopolytungstate, $W_{10}O_{32}^{4-}$, accessible with near UV or blue light, oxidize alkanes and conventionally far more reactive organic molecules including alcohols, alkenes, *N*-alkylacetamides, and ketones, at comparable rates. One or more of the latter three types of compounds are produced upon irradiation of acetonitrile solutions containing the polyoxotungstate and alkane substrate under anaerobic conditions. Comparison of alcohol versus alkane reactivities under absolute and competitive kinetic conditions indicates that alcohol-polyoxotungstate preassociation can be important in these processes. Reaction of *cis*- and *trans*-2-decalones in these systems indicates that functionalization of unactivated positions (primarily incorporation of the olefinic unit) remote from the usually activating ketone group can be accomplished.

Reference 8 extended this work and reported the catalytic functionalization of unactivated saturated C-H bonds in the presence of alcohol, ester, and ketone functional groups. The abstract is given below. This paper was cited in *The Scientist* as one of the most significant papers of 1989.

Abstract. The intrinsic kinetic selectivities exhibited in the oxidation of some classes of organic compounds by the excited states of polyoxometalates allows the development of methods based on these versatile and accessible inorganic complexes for the functionalization of alkanes in the presence of traditionally far more reactive substrates including alcohols and esters. These kinetic selectivities can be altered with the choice of reaction conditions, and in particular by the acidity of the medium. These kinetic selectivities facilitate, furthermore, the catalytic epimerization of an unactivated and saturated carbon center contained in a molecule, an aliphatic ketone, bearing conventionally far more reactive C-H bonds and functional groups elsewhere in the same molecule. This is the first process resulting in the modification of an unactivated C-H bond that proceeds both catalytically and at high conversion of substrate under mild conditions.

Reference 9 involved the delineation of another aspect of the photocatalytic activity of decatungstate, the ability to make carbanions directly from alkanes. This communication in JACS was also cited in *Chemical and Engineering News*. The abstract below summarizes the key points of the work.

Abstract. The isopolytungstate, $W_{10}O_{32}^{4-}$, catalyzes the photochemical functionalization of the strained caged hydrocarbon heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane, commonly referred to as HCTD, 1, under anaerobic conditions to produce the 1-acetyl derivative, $R(-H)COCH_3$, 2, an unprecedented replacement of an unactivated C-H bond with a C-C bond. Several other polyoxometalates of W and Mo are ineffective for this reaction. These acylation processes, (Table I) represent a one-electron oxidation of the carbon atom of the hydrocarbon, 1, and a one-electron reduction of the carbon atom of the acetonitrile; the net reaction is a nonredox process. A net redox process also takes place involving oxidation of the solvent (CH_3CN) and reduction of $W_{10}O_{32}^{4-}$. The reduced catalyst can be reoxidized by O_2 in the dark. Cycles of $W_{10}O_{32}^{4-}$ photoreduction followed by reoxidation can lead to production of 2 with selectivities and conversions that are not matched in any other biological radical process. Several experiments are in accord with the unprecedented C-C bond forming step being the generation and capture of small quantities of carbanion by the nitrile carbon followed by protonation and hydrolysis to yield 2. The products generated upon irradiation of 1 in the presence of O_2 are also unusual. The major products generated upon irradiation of adamantane under anaerobic conditions are the 1-acetyl adamantane, 1,3-diacetyl adamantane, and 1,3,5-triacetyl adamantane. The processes reported here break ground on several fronts.

Inasmuch as the use of O_2 as a terminal oxidant is of substantial importance in catalytic oxidative decontamination systems and in catalytic oxidation in general, we specifically sought to distinguish the role of photochemically active polyoxometalates as initiators of radical chain autoxidation. Some of the complexes are excellent initiators; others are not. Those that exhibit high quantum yields for the photooxidation step are generally quite effective. Our study in this area was published in *Inorganic Chemistry* (reference 7). The abstract follows.

Abstract. The photochemically active early transition metal polyoxometalate, decatungstate, $W_{10}O_{32}^{4-}$, in contrast to the conventional organic free radical chain initiators such as benzoyl peroxide and α,α' -azobis(isobutyronitrile), can initiate the autoxidation of isobutane using light of a sufficiently long wavelength (near UV and blue light), that the product *t*-butyl hydroperoxide is stable; furthermore, $W_{10}O_{32}^{4-}$, unlike conventional organic initiators is not consumed by the process of initiation. In addition, the autoxidation of isobutane can proceed with virtually quantitative selectivity in substrate conversions in excess of 50%.

References 6 and 11 are not publications as such reports or abstracts in the Proceedings of the 1988 and 1989 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense Research, respectively. Reference 6 describes one photochemical and one thermal system for the very rapid and complete oxidation of HD thioether analogues to the corresponding less toxic sulfoxides. The abstract for reference 6 is as follows.

Abstract. Two systems, one photochemical and one thermal, for the catalytic decontamination of dialkyl sulfide HD simulants are presented. The photochemical processes involve the irradiation of aqueous or acetonitrile solutions or suspensions of dialkyl sulfides and decatungstate with UV-visible light ($\lambda > 280$ nm) in the presence of dioxygen. The corresponding sulfoxides are the principal products. The thermal processes involve the oxidation of dialkyl sulfides with high selectivity and high conversion by *t*-butyl hydroperoxide (TBHP) catalyzed by heteropolytungstates substituted with d^0 VV ions.

The abstract for reference 11 is as follows.

Abstract. The selective oxidation of half mustard and other model thioethers by the *t*-butyl hydroperoxide (TBHP) / $H_5PV_2Mo_10O_{40}$ system to the corresponding sulfoxides has been examined in some detail. Rate studies with authentic thioethers, sulfoxides, and sulfones, and the isolation and characterization of a completely stable sulfoxide complex of the catalyst establish that sulfoxide is completely stable under the reaction conditions; absolutely no sulfone is produced. The substrate oxidation/polyoxometalate reduction process is the first and rate determining step in the overall mechanism. The oxidations are first order in thioether, second order in

polyoxometalate, variable order in H^+ and minimally sensitive to water. Photochemical catalytic oxidation of thioethers by polyoxometalates are not selective for production of sulfoxide; they facilitate C-S bond cleavage under some conditions leading to extensive oxidative degradation of thioethers.

Reference 16 is a very complete paper on the (TBHP) / $H_5PV_2Mo_{10}O_{40}$ thioether oxidation system. It is currently undergoing revision and will not be published for some time. The abstract is given below.

Abstract: The first metal-catalyzed oxidation of thioethers to sulfoxides with virtually quantitative selectivity for sulfoxide at high substrate conversion is reported (thioether + ROOH \rightarrow sulfoxide + ROH). Vanadium-substituted heteropoly acids are the catalysts and *t*-butyl hydroperoxide (TBHP), the oxidant. Unlike all other reported stoichiometric or metal-catalyzed thioether oxidations, further oxidation of the sulfoxide products to the sulfone can be rendered kinetically insignificant in these systems and a stable complex between an exemplary sulfoxide, tetrahydrothiophene oxide (THTO) and one of the better catalysts for these oxidations, $H_5PV_2Mo_{10}O_{40}$, 1, with formula $(THTO\cdot H^+)_4(H^+)(PV_2Mo_{10}O_{40}^{5-})$, 2, has been both isolated from catalytic systems and prepared independently. The experimental tractability of one system, oxidation of tetrahydrothiophene (THT) by TBHP catalyzed by 1, was such that sufficient kinetics and spectroscopic information could be obtained to establish several key features of the mechanism and the direct role of polyoxometalate protonation state in the reactivity and selectivity exhibited in such oxidations. The net reaction is constituted by two principal processes, direct oxidation of the thioether by 1, and subsequent reoxidation of the resulting reduced polyoxometalate by TBHP. The substrate oxidation/polyoxometalate reduction process is first order in thioether, second order in polyoxometalate, variable order in H^+ and minimally sensitive to water. The substrate activation step most likely involves electron transfer from the thioether sulfur to one of two molecules of 1 in the rate determining transition state. Reoxidation of the reduced complex, $PV_2Mo_{10}O_{40}^{5-}$, by TBHP is considerably less complex: first order in both the reduced complex and TBHP. The mechanistic information permits a rational and simple method, manipulation of polyoxometalate protonation state, to control the selectivity-determining ratio of rates in the thioether oxidations, $k_{\text{thioether}}[\text{thioether}][\text{oxidant}] / k_{\text{sulfoxide}}[\text{sulfoxide}][\text{oxidant}]$ and other features of the reaction.

References 12 and 13 report two new processes pertinent to the degradation of thioethers such as HD: oxidative C-H bond cleavage and reductive C-S bond cleavage in the same reaction catalyzed by $W_{10}O_{32}^{4-}$. Reference 12 is not a publication but an report or abstract to the CRDEC Conference on Chemical Defense Research. The abstract is as follows.

Abstract. Polyoxometalates catalyze the photochemical oxidative degradation of thioether mustard analogues under both aerobic and anaerobic conditions. Under aerobic conditions, degradation is complete. Irradiation under anaerobic conditions results in two novel processes, C-H bond activation and C-S bond cleavage. C-H bond activation derives from oxidation of the thioether, while C-S bond cleavage derives from reduction of the thioether. The anaerobic photochemical oxidation of thioethers by decatungstate is first order in complex and light, and variable order in substrate. Decatungstate is more reactive than other polyoxometalate species because of its increased visible light absorption and higher quantum yields.

Reference 13 is a full paper in the *Journal of the American Chemical Society* on this system. The abstract summarizing the work is as follows.

Abstract. Several experiments examining the photooxidation of thioethers by polyoxotungstates have established that the less oxidizing photochemically active complex, $W_{10}O_{32}^{4-}$, but not the more oxidizing photochemically active heteropolytungstates such as α - $PW_{12}O_{40}^{3-}$ can be used to effect both substrate photooxidation and reduction in the same reaction. Under anaerobic conditions in solution at ambient temperature the excited state of $W_{10}O_{32}^{4-}$ reacts with thioethers in high selectivity by α hydrogen abstraction to form the α carbon radicals. Neither photooxidation by electron transfer to generate the thioether cation radicals nor production of the conventional oxygenated products, sulfoxide and sulfone, are seen in these reactions. The principal reduced form of the catalyst, $W_{10}O_{32}^{6-}$, reduces thioethers to effect C-S bond cleavage, thus the net observed products in anaerobic photooxidation of these substrates catalyzed by $W_{10}O_{32}^{4-}$ are the dimers resulting from coupling of the α -carbon radicals and C-S bond cleavage products including the hydrocarbon resulting from complete desulfurization of the thioether. The only important processes exhibited by the excited state, $W_{10}O_{32}^{4-*}$, under conditions where background photooxidation of CH_3CN solvent is not significant ($[thioether] > 25$ mM) are attack on thioether substrate, k , and unimolecular radiationless decay, k_{rd} . The rate law for production of the readily monitored inorganic product, $W_{10}O_{32}^{6-}$, (Rate = $k\phi I[R_2S]/k[R_2S] + k_{rd}$) is consistent with the kinetically competent excited state, $W_{10}O_{32}^{4-*}$, being produced by absorption of one photon of near UV light and rate limiting attack of this species on thioether. Under aerobic conditions, $W_{10}O_{32}^{4-}$ catalyzes the complete oxidative conversion of thioethers principally to sulfoxides and sulfones by a complicated process that involves, in part, radical chain autoxidation. Sulfoxides readily quench the photoredox active excited state of $W_{10}O_{32}^{4-}$ ($k_{qt} = 9.4$ M⁻¹).

Next, we developed systems for the catalytic dehalogenation of toxic halocarbons such as HD. Only the first paper on this subject as appeared at this time, reference 10. The abstract to this communication is as follows.

Abstract. Some polyoxotungstates, and in particular $W_{10}O_{32}^{4-}$, catalyze the reductive dehalogenation of carbon tetrachloride by alcohols upon irradiation under either aerobic or anaerobic conditions.

Reference 14 is an extension of this work, but I will not give the abstract of this manuscript and discuss it as it stands as we plan to completely rewrite rewrite it and submit it to *Journal of the American Chemical Society*.

Finally, we did a thorough comparison of semiconductor metal oxides and polyoxometalates as photocatalysts for oxidative degradation. The abstract for this paper, reference 15, is as follows. This paper is undergoing revision and is not yet satisfactory for publication in our view. The final version will be submitted soon.

Abstract. The photochemical degradation of thioether substrates catalyzed by representative semiconductor metal oxides (anatase TiO_2 , SnO_2 , cubic WO_3 , and CdS) and photoredox active early transition metal polyoxometalates ($W_{10}O_{32}^{4-}$, $PMo_{12}O_{40}^{3-}$, $PW_{12}O_{40}^{3-}$, $SiMo_{12}O_{40}^{4-}$, $PV_2Mo_{10}O_{40}^{5-}$, $Cu^{II}W_{11}PO_{39}^{5-}$, and $P_2W_{18}O_{62}^{6-}$) have been examined under both anaerobic and aerobic conditions. Under anaerobic conditions, all the semiconductors are completely ineffective at photochemically oxidizing or degrading the exemplary thioether substrate tetrahydrothiophene (THT) in the oxidatively resistant solvent acetonitrile. In contrast, all the homogeneous polyoxometalate systems under the same reaction conditions except the neutral tetra-*n*-butylammonium (Q) salt of $PW_{12}O_{40}^{3-}$, are quite effective. The latter systems generate products derived from the carbon-based radical α to the sulfur atom and not sulfoxide or sulfone, the usual products of thioether oxidation by oxometal species. The rate for the most active anaerobic system, that involving the photochemical degradation of THT by $Q_4W_{10}O_{32}$, under optically dilute conditions, is first order in $W_{10}O_{32}^{4-}$ and light intensity and variable order in THT substrate. The simple rate law ($v = +d/dt[W_{10}O_{32}^{6-}] = k\phi I[THT]/k[THT] + k_{10}$) is consistent with this data and the observation of saturation kinetics in THT. Upon addition of O_2 , TiO_2 (with or without $Pt(0)$) becomes highly active, SnO_2 becomes active, but WO_3 and CdS remain inactive. Reactivity in thioether oxidation is dominated by the interactions of the semiconductors with O_2 and O_2 derived intermediates; there is no correlation between reactivity and semiconductor band gap. Upon addition of O_2 , all the polyoxometalate systems become more active. The most active catalyst on a mole (g-atom) basis for decomposing thioethers in the presence of air is the polyoxometalate $Q_4W_{10}O_{32}$; TiO_2 anatase (Degussa P 25) is the most active semiconductor. Both the semiconductors and polyoxometalates under aerobic conditions oxidize thioethers further than the sulfoxides or sulfones to a range of products.

C. List of all publications and technical reports. References 1 and 2 are accounts of early decontamination done with CRDEC staff 3 years ago that did not cite ARO support as such. References 3-16 are derived from our ARO funded work.

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(12) Hill, C. L.; Chambers, R. C. "Photocatalytic C-H and C-S Bond Cleavage in Mustard Analogues" Proceedings of the 1989 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense Research. US Army Armament, Munitions & Chemical Command, 1990, pp xxx-xxx, (being compiled).

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D. List of all participating scientific personnel

- (1) Robert B. Brown Jr. (supported very briefly full time at the very beginning of the contract; PhD granted in 1988)
- (2) Lucille A. Combs-Walker (full time on project for a limited period)
- (3) Miryam Kadkhodayan (full time over a brief period, PhD awarded in early 1990, now postdoctoral fellow at U.C. Berkeley)
- (4) Robert Carlisle Chambers, (the only student who was supported full time on the project throughout most of its duration; he will obtain his PhD in mid-1991).
- (5) Mahmoud Faraj (part time for a few months)
- (6) Daryush Sattari (part time for roughly the last half of contract)

List of inventions. No patents filed thus far.